Synthesis of end-group functionalized P3HT: general protocol for P3HT/nanoparticle hybrids

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KEYWORDS

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ABSTRACT

Poly(3-hexylthiophene)s were synthesized with phosphonic ester, pyridine, thiol and phenol end-groups using functionalized air-stable Ni-initiators. The protected thiol and phenol functionalized P3HTs were converted in thiol- and phenol P3HTs by quantitative postpolymerization reactions.

^{1}H NMR and MALDI-ToF analysis showed very high degrees of functionalization and strong control over the polymerization except for the pyridine functionalized P3HT. These functional end-groups were used to prepare hybrid materials from a broad variety of nanoparticles, including metal oxides, quantum dots and noble metals.

INTRODUCTION

While conjugated polymers (CPs) were initially ill-defined materials that were not suited for (advanced) applications, they have evolved into state-of-the-art macromolecules with dedicated molecular structure driving modern and future applications. A milestone in this process was the discovery of the controlled chain-growth polymerization of poly(3-alkylthiophene)s (P3AT)s,[1–4] later also applied to some other conjugated polymers.[5–11] This controlled polymerization procedure allows synthesizing CPs with predictable molar masses, low polydispersities and perfect control of the molecular structure. Moreover, it also provides the possibility to prepare all-conjugated block copolymers by successive monomer addition[12–33] with a great control on the end-groups. When Ni(dppp)Cl_2 is used as the catalyst/initiator, H/Br-terminated CPs are obtained.[3,4] The synthesis of CPs bearing other end-groups is nowadays readily achieved and can be accomplished in three ways. Firstly, the controlled chain-growth polymerization can be exploited by addition of a Grignard reagent equipped with a functional group.[34–37] The drawback of this approach is that it requires a controlled polymerization, which is only the case for a selected number of CPs. This method also suffers from the fact that, depending on the nature of the functional group, both mono- and dicapping occur[34–37], although the presence of additives was shown to help increasing the fraction of monocapped polymers. By the way, the sample is also often contaminated with polymers lacking the functional group.[36,37] The second approach to introduce a functional end-group is based on a postpolymerization reaction. For instance,

Langeveld-Voss *et al* managed to convert the Br-atom to an H-atom or a trimethylsilyl group by addition of a Grignard reagent in the presence of Ni(dppp)Cl_2.[338] Alternatively, the Br-atom can be converted into MgCl by a GRIM reaction using *i*-PrMgCl. In a subsequent step, the organometallic group can react with CO_2 yielding the corresponding carboxylic acid derivative.[39] An aldehyde function can also be introduced at the H-terminated thiophene moiety by applying the Vilsmeier reaction.[40] The third strategy relies on the use of Ni-initiators equipped with a functional group. Such a protocol can be more generally applied, since it does not require a controlled polymerization. On the other hand, if the polymerization is controlled, this approach exclusively results in polymer chains end-capped with the functionalized initiator on one end and an H-atom on the other (if terminated with acid). For instance, Luscombe's group prepared phosphonic ester-functionalized initiators *in situ* and applied them in the polymerization of P3HT. However, since the initiators were not isolated and purified prior to the polymerization process, polymer chains lacking the functional group were obtained.[41] Kiriy and coworkers prepared and used an alkoxy initiator[42] and an initiator bearing a benzothiadiazole.[43] The group of Verduzco used a protected alcohol functional initiator.[44] Finally, our group prepared and isolated Ni-initiators equipped with (protected) acetylene, alcohol, carboxylic acid and amine groups.[45,46]

One of the main advantages of CPs equipped with a functional end-group is the possibility to synthesize interesting conjugated block copolymers which might not be prepared be conventional successive monomer addition.[44,46,47] Another asset is that they can be used to decorate nanoparticles (NPs). For instance, Kochemba *et al* used pyridine end-capped P3HT to ligate CdSe nanodots and demonstrated that an increased stability of the morphology is found.[36]

In the present manuscript, we report on the preparation and the use of new Ni-initiators functionalized with phosphonic ester, pyridine, (protected) phenol and (protected) thiol groups. The successful introduction of such functional groups as end-group in P3HTs (Figure 1), followed by deprotection procedures, leads to the preparation of original functionalized P3HTs. Those CPs are then used to decorate a broad variety of NPs based on a grafting-to method. The different functional groups have been then selected to allow preparing a very broad variety of CP/NP hybrid materials.

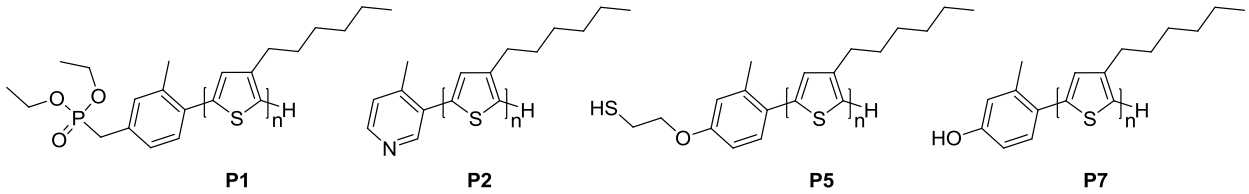


Figure 1. Structures of the end-group functionalized P3HTs.

EXPERIMENTAL SECTION

Reagents and Instrumentation

All reagents were purchased from TCI, Sigma-Aldrich, Acros Organics and ABCR. CdSe/ZnS quantum dots were purchased from Evident Technologies (Evidots, ED-C11-TOL-0520). Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). The gel permeation chromatography (GPC) measurements were performed using a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran as eluent calibrated toward polystyrene standards. ^{1}H nuclear magnetic resonance (^{1}H NMR) measurements were carried out with a Bruker Avance 300, 400 and 600 MHz. ^{31}P NMR measurents were carried out with a Bruker Avance 400 MHz.

Mass spectra were recorded using an Agilent HP5989. The compounds are ionized by electron impact (EI). Matrix-assisted laser desorption ionization-time-of-flight (MALDI-ToF) mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser of 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10 000. The matrix, trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]malonitrile (DCTB), was prepared as a 40 mg/mL solution in chloroform.[48] The matrix solution (1 μL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in chloroform to obtain 1 mg/mL solutions. Then, 1 μL aliquots of these solutions were applied onto the target area (already bearing the matric crystals) and then air-dried. IR spectra were recorded using a Bruker Alpha-p apparatus in ATR mode. UV-vis measurements were performed on a Perkin-Elmer Lambda 900 UV-vis NIR.

4-Bromo-3-methylbenzylalcohol (**1**)[45] and 2-(4-bromo-3-methylphenoxy)ethanol (**7**)[46] were prepared according to literature procedures. *N*-octylamine coated iron oxide nanoparticles were synthesized using a modified forced hydrolysis method.[49] Gold nanoparticles were produced using a modified Turkevich citrate reduction method.[50]

Synthesis of the phosphonic ester initiator

*Synthesis of **2***. A solution **1** (18,0 mmol, 3.62 g) in CH_2Cl_2 (100 mL) was put under argon atmosphere, shielded from light, cooled to 0°C and *N*-bromosuccinimide (NBS) (22.5 mmol, 5.95 g) was added portion wise. The mixture was allowed to react at room temperature overnight, after which aqueous $NaHSO_3$ and NaOH were added. The mixture was extracted with CH_2Cl_2, the organic layer was dried over $MgSO_4$ and filtered. Subsequently, the solvent was

removed under reduced pressure. Finally, the crude product was purified by column chromatography (SiO_2, eluent: CH_2Cl_2/EtOAc/heptane 4/3/3) and isolated as a colorless oil.

Yield: 3.47 g (73%)

^{1}H NMR ($CDCl_3$): δ = 7.49 (d, 1 H, J = 8.1 Hz), 7.25 (d, 1 H, J = 2.2 Hz), 7.07 (dd, 1H, J = 8.1 Hz, J = 2.2 Hz), 4.42 (s, 2 H), 2.39 (s, 3 H)

^{13}C NMR ($CDCl_3$): δ = 138.5, 137.0, 132.8, 131.4, 127.9, 125.0, 32.6, 22.9

MS: *m/z* = 262 (M^+)

*Synthesis of **3***. **2** (2.70 mmol, 713 mg) was brought under argon atmosphere and added to triethylphosphite (8.10 mmol, 1.30 mL). The mixture was refluxed for 32 h after which the product was purified by column chromatography (SiO_2, eluent: CH_2Cl_2/MeOH 95/5) and isolated as a colorless oil.

Yield: 702 mg (81%)

^{1}H NMR ($CDCl_3$): δ = 7.46 (d, 1 H, J = 8.1 Hz), 7.17 (s, 1 H), 6.97 (d, 1H, J = 8,1 Hz), 4.03 (m, 4 H), 3.07 (d, 2 H, J = 21.5 Hz), 2.37 (s, 3 H), 1.26 (t, 6 H)

^{13}C NMR ($CDCl_3$): δ = 138.0, 132.4, 132.2, 131.0, 128.7, 123.4, 62.2, 33.1, 22.9, 16.4

MS: *m/z* = 320 (M^+)

*Synthesis of **4***. A solution of **3** (2.00 mmol, 642 mg) in dry toluene (70 mL) was added under argon atmosphere to $Ni(PPh_3)_4$ (1.50 mmol, 1.66 g). After reacting overnight the solution was

filtered. The supernatant was concentrated and the product was precipitated in 600 mL of pentane. Finally, the product was dried and obtained as a yellow powder.

Yield: 393 mg (29%)

^{1}H NMR (CD_2Cl_2): δ = 7.61-7.10 (m, 30 H), 7.05 (s, 1 H), 6.23 (s, 1 H), 5.95 (s, 1 H), 4.05 (m, 4 H), 2.73 (d, 2 H, J = 20.6 Hz), 1.97 (s, 3 H), 1.26 (m, 6 H)

^{31}P NMR ($CDCl_3$): δ = 29.73, 21.61

Synthesis of the pyridine initiator

*Synthesis of **6***. The same procedure was used as for the synthesis of **4**, but this time the product **6** was precipitated in heptane (500 mL) and washed with pentane (100 mL). The used reagents were **5** (2.27 mmol, 391 mg) and $Ni(PPh_3)_4$ (1.70 mmol, 1.88 g).

Yield: 206 mg (12%)

^{1}H NMR (CD_2Cl_2): δ = 9.35 (s, 1 H), 7,75 (m, 12 H), 7.40 (m, 18 H), 5.83 (m, 2 H), 2.51 (s, 3 H)

^{31}P NMR ($CDCl_3$): δ = 30.45

Synthesis of thiol initiator

*Synthesis of **8***. A solution of **7** (6.00 mmol, 1.39 g) and PPh_3 (7.50 mmol, 1.96 g) in CH_2Cl_2 (50 mL) was put under argon atmosphere, shielded from light, cooled to 0 °C and NBS (7.50 mmol, 1.34 g) was added portion wise. The mixture was allowed to react at room temperature overnight after which aqueous $NaHSO_3$ and NaOH were added. The mixture was extracted with CH_2Cl_2, the organic layer was dried over $MgSO_4$ and filtered. Subsequently, the solvent was removed

under reduced pressure. Finally, the crude product was purified by column chromatography (SiO_2, eluent: heptane/EtOAc 7/3) and isolated as a colorless oil.

Yield: 1.57 g (89%)

^{1}H NMR ($CDCl_3$): δ = 7.40 (d, 1 H, J = 8.8 Hz), 6.81 (d, 1 H, J = 3.0 Hz), 6.62 (dd, 1 H, J = 8.8 Hz, J = 3.0 Hz), 4.25 (t, 2 H), 3.62 (t, 2 H), 2.37 (s, 3 H)

^{13}C NMR ($CDCl_3$): δ = 157.3, 139.1, 133.0, 117.4, 116.2, 113.7, 68.0, 29.0, 23.1

MS: *m/z* = 292 (M^+)

Synthesis of ***9***. *n*-BuLi (3.50 mmol, 1.40 mL) was added to a solution of tri(*iso*-propyl)silylthiol (3.50 mmol, 667 mg) in dry THF (10 mL) under argon atmosphere at 0°C. The mixture was allowed to react during 15 minutes and subsequently transferred to a solution of **8** (1.77 mmol, 521 mg) in dry THF (50 mL). After reacting overnight, H_2O was added and the mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the crude product was purified by column chromatography (SiO_2, eluent: heptane/ EtOAc 8/2) and isolated as a colorless oil.

Yield: 621 mg (87%)

^{1}H NMR ($CDCl_3$): δ = 7.39 (d, 1 H, J = 9.0 Hz), 6.79 (d, 1 H, J = 2.7 Hz), 6.59 (dd, 1 H, J = 9.0 Hz, J = 2.7 Hz), 4.04 (t, 2 H), 2.88 (t, 2 H), 2.35 (s, 3 H), 1.26 (m, 3 H), 1.13 (d, 18 H)

^{13}C NMR ($CDCl_3$): δ = 132.9, 117.1, 115.7, 113.6, 77.2, 69.3, 24.4, 23.1, 18.5, 12.7, 0.0

MS: *m/z* = 402 (M^+), 360 (M^+ - *i*-Pr)

*Synthesis of **10***. The same procedure was used as for the synthesis of **4**, but this time the product **10** was precipitated in hexane (500 mL) and washed with pentane (100 mL). The used reagents were **9** (2.05 mmol, 827 mg) and $Ni(PPh_3)_4$ (1.53 mmol, 1.70 g).

Yield: 520 mg (31%)

^{1}H NMR (CD_2Cl_2): δ = 7.52 (m, 12 H), 7.31 (m, 6 H), 7.23 (m, 12 H), 6.80 (d 1 H, J = 8.5 Hz), 5.98 (d, 1 H, J = 8.5 Hz), 5.66 (s, 1 H), 3.72 (t, 2 H), 2.74 (t, 2 H), 2.04 (s, 3 H), 1.25 (m, 3 H), 1.11 (d, 18 H)

^{31}P NMR ($CDCl_3$): δ = 22.09

Synthesis of phenol initiator

*Synthesis of **12***. *tert*-Butyl(dimethyl)silyl chloride (6.25 mmol, 937 mg) in CH_2Cl_2 (7 mL) was added to a mixture of 4-bromo-3-methylphenol **11** (5.00 mmol, 935 mg) and imidazole (7.50 mmol, 510 mg) in CH_2Cl_2 (10 mL) under argon atmosphere. After full conversion, H_2O was added and the compound was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the product was obtained as a colorless oil.

Yield: 1.30 g (86%)

^{1}H NMR ($CDCl_3$): δ = 7.32 (d, 1 H, J = 8.4 Hz), 6.72 (s, 1 H), 6.54 (d, 1 H, J = 8.4 Hz), 2.32 (s, 3 H), 0.96 (s, 9 H), 0.17 (s, 6 H)

^{13}C NMR ($CDCl_3$): δ = 154.9, 138.8, 132.8, 122.6, 119.1, 116.2, 25.6, 23.0, 18.2, -4.5

MS: *m/z* = 300 (M^+)

*Synthesis of **13***. The same procedure was used as for the synthesis of **10**. The used reagents were **12** (2.00 mmol, 602 mg) and $Ni(PPh_3)_4$ (1.50 mmol, 1.66 g).

Yield: 396 mg (27%)

^1H NMR (CD_2Cl_2): δ = 7.49 (m, 12 H), 7.31 (m, 6 H), 7.23 (m, 12 H), 6.85 (d 1 H, J = 8.4 Hz), 5.89 (d, 1 H, J = 8.4 Hz), 5.58 (s, 1 H), 1.97 (s, 3 H), 0.87 (m, 9 H), 0.09(s, 6 H)

^{31}P NMR ($CDCl_3$): δ = 21.63

General procedure for the synthesis of the polymers P1, P2, P3, P6

The initiators **4**, **6**, **10** or **13** (50,0 μmol) and dppp (100 μmol, 41.2 mg) were dissolved in dry THF (4 mL), purged with argon and stirred for 10 minutes. Subsequently, monomer **15** in dry THF (8.67 mL) was added to the initiator solution. For the synthesis of **15**, the precursor monomer **14** (1 mmol, 373 mg) was dissolved in dry THF (8 mL), purged with argon and *i*-PrMgCl.LiCl (1.28 M in THF, 1.00 mmol, 0.87 mL) was added to the solution. The reaction was stirred during 15 minutes at 40°C and another 45 minutes at room temperature. To verify the conversion a small aliquot (0.2 mL) was quenched with D_2O and analyzed by ^1H NMR. After polymerizing for 1 h, the reaction mixture was quenched with a 2 M HCl solution. The mixture was concentrated and the polymer was precipitated in MeOH. Next, the polymer was filtered and fractionated by Soxhlet extraction with methanol, acetone and chloroform. The chloroform fraction was concentrated and the polymer was precipitated in methanol, filtered and dried in vacuo. Aal polymers were isolated as a dark red-brown solid.

*Synthesis of **P1***. Initiator **4** (50.0 μmol, 45.2 mg) was used. Yield: 129 mg (78%)

*Synthesis of **P2**.* Initiator **6** (50.0 µmol, 37.8 mg) was used. Yield: 119 mg (72%)

*Synthesis of **P3**.* Initiator **10** (50.0 µmol, 49.3 mg) was used. Yield: 123 mg (74%)

*Synthesis of **P6**.* Initiator **13** (50.0 µmol, 44.2 mg) was used. Yield: 135 mg (81%)

Postpolymerization reactions

*Synthesis of **P5**.* Under argon atmosphere, TBAF was allowed to react with HCl for 15 minutes, after which the reaction mixture was added to a solution of **P3** (120 µmol, 20 mg) in THF (50 mL). After full conversion, the mixture was concentrated and the polymer was precipitated in methanol, filtered and purified by a Soxhlet extraction with aceton and chloroform. The chloroform was then removed from the chloroform-soluble fraction. THF was added to the polymer and purged with argon, after which tributylphosphine (1.20 mmol, 0.30 mL) and 38% HCl (1.20 mmol, 0.10 mL) was added to the solution to reduce the formed disulfides. The reduction was monitored with GPC. After a 3 h, the reaction mixture was concentrated and precipitated in methanol, filtered and dried in vacuo. The final polymer was a dark red-brown solid.

Yield: 19.2 mg (96%)

*Synthesis of **P7**.* A solution of **P6** (120 µmol, 20,0 mg) in THF (20 mL) was purged with argon and shielded from light. TBAF.$3H_2O$ (1.20 mmol, 379 mg) was added and the reaction was stirred overnight. After full conversion, the mixture was concentrated and the polymer was precipitated in methanol, filtered and purified by a Soxhlet extraction with aceton and chloroform. The chloroform fraction was concentrated, precipitated in methanol, filtered and dried in vacuo. The final polymer was a dark red-brown solid.

Yield: 19.6 mg (98%)

Synthesis of the hybrid P3HT/nanoparticles

*Synthesis of **H1***. Dry *N*-octylamine coated iron oxide nanoparticles (10 mg) were dispersed in chloroform (5 mL) using ultrasonication for 1.5 h. In another flask, **P1** (60.0 μmol, 10 mg) was dissolved in chloroform (1 mL). Then 2.5 mL of the 2 mg/mL iron oxide nanoparticle dispersion was mixed with the **P1** solution in the ultrasonicator and after mixing, the dispersion was ultrasonicated for another 48 h. Purification of the hybrids was done by magnet-assisted precipitation and redispersion in chloroform followed by two washing steps with acetone. The final product was dispersed in chloroform.

*Synthesis of **H2.*** Using ultrasonication, **P2** (52.2 μmol, 8.7 mg) was dissolved in toluene (4 mL). Sonication was applied for 30 minutes to ensure optimal dissolution. Then, 0.5 mL of a 10 mg/mL dispersion of CdSe/ZnS quantum dots in toluene was added to the **P2** solution while in the ultrasonicator. The mixture was left in the ultrasonicator for 100 h. After this period, the dispersion was centrifugated at 6000 rpm for 10 minutes, forming a pellet at the bottom of the flask. This pellet was then redispersed in toluene. The process of centrifugation and redispersion was repeated twice to obtain the final, purified product.

*Synthesis of **H3.*** In a flask, **P5** (45.0 μmol, 7.5 mg) was dissolved in chloroform (3 mL) using ultrasonication. When **P5** was completely dissolved, 10 mL of the aqueous gold nanoparticle dispersion was added. To enable capping of the hydrophilic gold nanoparticles by the hydrophobic **P5**, tetraoctylammonium bromide (80 mM in chloroform, 5 mL) was added as phase transfer agent. The mixture was then sonicated 48 h. After reaction, the nanoparticles were purified using centrifugation at 10 000 rpm for 15 minutes and were redispersion in chloroform.

*In situ synthesis of **H4.*** An aqueous $HAuCl_4$ solution (30.0 mM, 3.5 mL) was mixed with tetraoctylammonium bromide solution in chloroform (50.0 mM, 9.41 mL). The flask was then put in an ultrasonicator until all $HAuCl_4$ was transferred from the aqueous to the chloroform phase, which is visible through a clear color change. A solution of **P7** (42.0 μmol, 7.00 mg) in chloroform (1 mL) was added to the mixture, followed by the addition of an aqueous sodium borohydride solution (2.94 mL, 400 mM). The reaction mixture was then left in the ultrasonicator for 3 h. Afterwards, the mixture was purified through centrifugation at 6000 rpm for 10 minutes and redispersion in chloroform.

RESULTS AND DISCUSSION

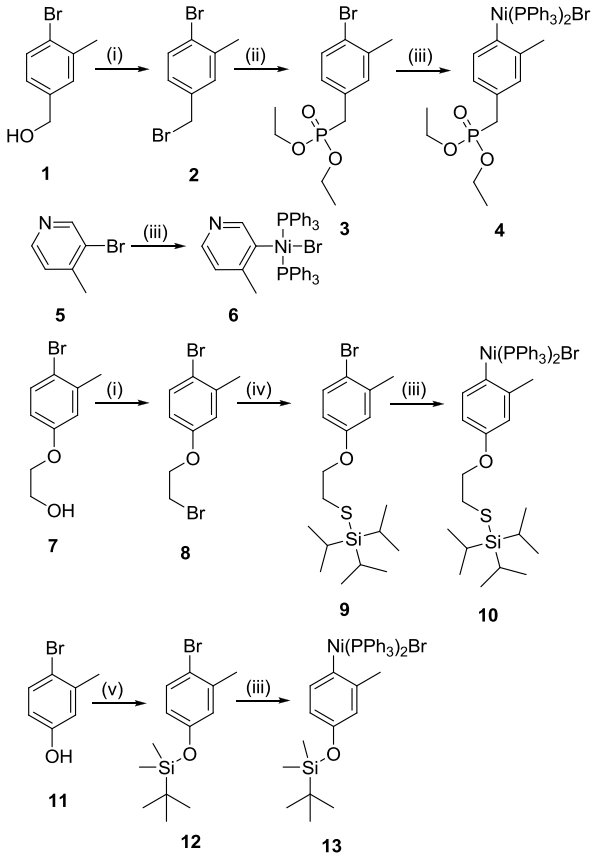
Synthesis of the Ni-initiators

The functional Ni-initiators were prepared by a oxidative insertion of $Ni(PPh_3)_4$ in an appropriately functionalized *o*-tolylbromide. The *o*-tolyl group was used to enhance the stability against disproportionation. As already mentioned, four different functional groups are investigated: phosphonic ester, pyridine, thiol and phenol. Since the monomers employed in the polymerization reaction are Grignard reagents, protection of the acidic phenol and thiol initiator functionalities is a necessity.

The overview of all synthetic steps for the synthesis of the functionalized initiators is presented in Scheme 1. The synthesis of the phosphonic ester initiator starts with an Appel reaction with NBS and PPh_3 in CH_2Cl_2 to prepare 4-bromo-3-methylbenzylbromide (**2**). The bromide (**2**) is then converted to a phosphonic ester using an Arbuzov reaction with triethylphosphite to yield 4-bromo-3-methylbenzyldiethylphosphonate (**3**). $Ni(PPh_3)_4$ undergoes an oxidative insertion with **3** in toluene, in order to form the phosphonic ester initiator (**4**). In the same vein, the preparation of

the pyridine initiator (**6**) is readily performed by reacting $Ni(PPh_3)_4$ with commercially available **5** in toluene. As a third end-group a thiol was chosen. For the actual polymerization, the thiol functionality was protected with tri(*iso*-propyl)silane (TIPS). Thus, **7** was converted to **8** using NBS with PPh_3 in CH_2Cl_2 in an Appel reaction. Afterwards the bromine function was converted to the thiolTIPS (**9**) functionality by a substitution with *i*-Pr_3SiSLi, prepared by a reaction of *i*-Pr_3SiSH with *n*-BuLi. The addition of **9** in toluene to $Ni(PPh_3)_4$ resulted in the initiator **10**. Finally, a phenol initiator was synthetized. The phenol initiator was protected by *tert*-butyldimethylsilane (TBDMS) group. Thus, 4-bromo-3-methylphenol (**11**) was converted with *tert*-butyldimethylsilyl chloride and imidazole in CH_2Cl_2 to **12**. Finally, **12** was added to $Ni(PPh_3)_4$ to form the protected phenol initiator **13**.

Scheme 1. Synthesis of the Ni initiators.[a]

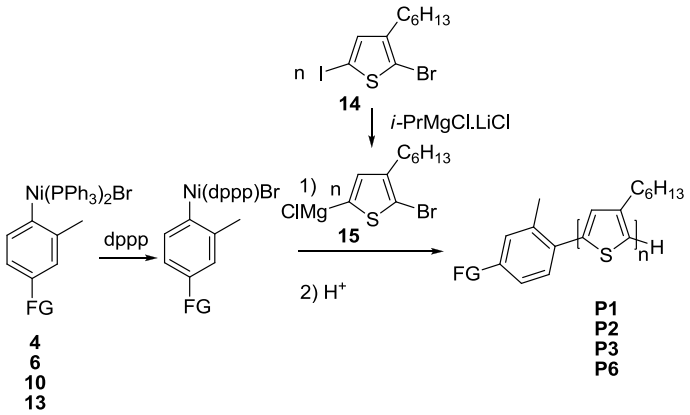


[a]Conditions: (i) NBS, PPh_3; (ii) $P(OEt)_3$; (iii) $Ni(PPh_3)_4$; (iv) HSTIPS, *n*-BuLi; (v) TBDMSCl, imidazole.

Synthesis of the polymers

All polymers were synthesized following a Ni(dppp)-mediated Kumada catalyst transfer polycondensation (KCTP) (Scheme 2). Thus, the precursor monomer 2-bromo-5-iodo-3-hexylthiophene (**14**) was converted to the actual monomer 5-magnesiochloro-2-bromo-3-hexylthiophene (**15**) using *i*-PrMgCl.LiCl. Prior to initiation, a ligand exchange using 2 eq. of 1,3-bis(diphenylphosphino)propane (dppp) is performed on the initiator,[45] because this ligand, in contrast to PPh_3, results in a living polymerization. As a direct consequence, the degree of polymerization can be tuned by varying the $[M_0]/[In]$ ratio. This value was set to 20 for all the polymerizations. The polymerization was terminated after 1 h by quenching the mixture with a 2 M HCl solution in THF.

Scheme 2. Synthesis of the polymers.



The molar mass and polydispersities of **P1**, **P2**, **P3** and **P6** (Table 1) were determined with GPC toward polystyrene standards. It is important to keep in mind that GPC tends to overestimate the

molar mass of polythiophenes.[48,51] This also explains the higher DP obtained by GPC than the absolute DP calculated from ^{1}H NMR (see also further). Except for the pyridine functionalized **P2** (see also further), low polydispersities were obtained, in line with the controlled nature of the polymerization.

Table 1. $\overline{M_n}$, PDI and DP for **P1**, **P2**, **P3** and **P6**.

Polymer	$\overline{M_n}$ (kg/mol)[a]	DP[a]	PDI[a]	DP[b]
P1	5.0	29	1.2	21
P2	7.5	44	1.4	46
P3	4.1	24	1.2	16
P6	4.6	27	1.1	17

[a] determined by GPC in THF toward polystyrene standard

[b] determined by ^{1}H NMR

^{1}H NMR and MALDI-ToF analysis

A magnification of the ^{1}H NMR and MALDI-ToF spectra of P1 (Figure 2, for complete spectra, see supplementary info, Figure S27) shows the resonance signal of the *o*-tolyl function of the initiator function at 2.48 ppm (**a**), a large peak originating from the internal α-methylene protons (**b**) and a triplet that originates from the terminal α-methylene (**c**). The ppm-value (2.61, **c**) of the α-methylene protons corresponds to the α-methylene protons of H-terminated thiophene units – α-methylene protons of Br-terminated thiophene resonates at 2.57 ppm,[29,52] which is not observed in the ^{1}H NMR spectrum – demonstrating that all chains were living when the polymerization was terminated. The fact that both the initiator and the α-methylene signals present similar integration values points to a quantitative initiation. The DP was calculated using the integration of the inner (**b**) and terminal (**c**) α-methylenes, resulting in a DP of 21.

The DP thus obtained by NMR integration fully correlates with the DP (i.e. 20) which would be expected for a controlled polymerization. Furthermore, it can be concluded that GPC does indeed overestimate the molar mass of P3HTs when calibrated towards PS standards.

MALDI-ToF analysis of P1 (Figure 2) shows that all chains were indeed initiated by the external initiator and that the polymers were mainly phosphonic ester/H terminated, but that also a small amount of the chains were phosphonic ester/Br terminated. This Br-termination probably originates from a spontaneous dissociation of the Ni-entity from the polymer chain, resulting in early termination. Transfer reactions of the propagating Ni-catalyst were not observed, since no H/Br terminated P3HT chains were found.

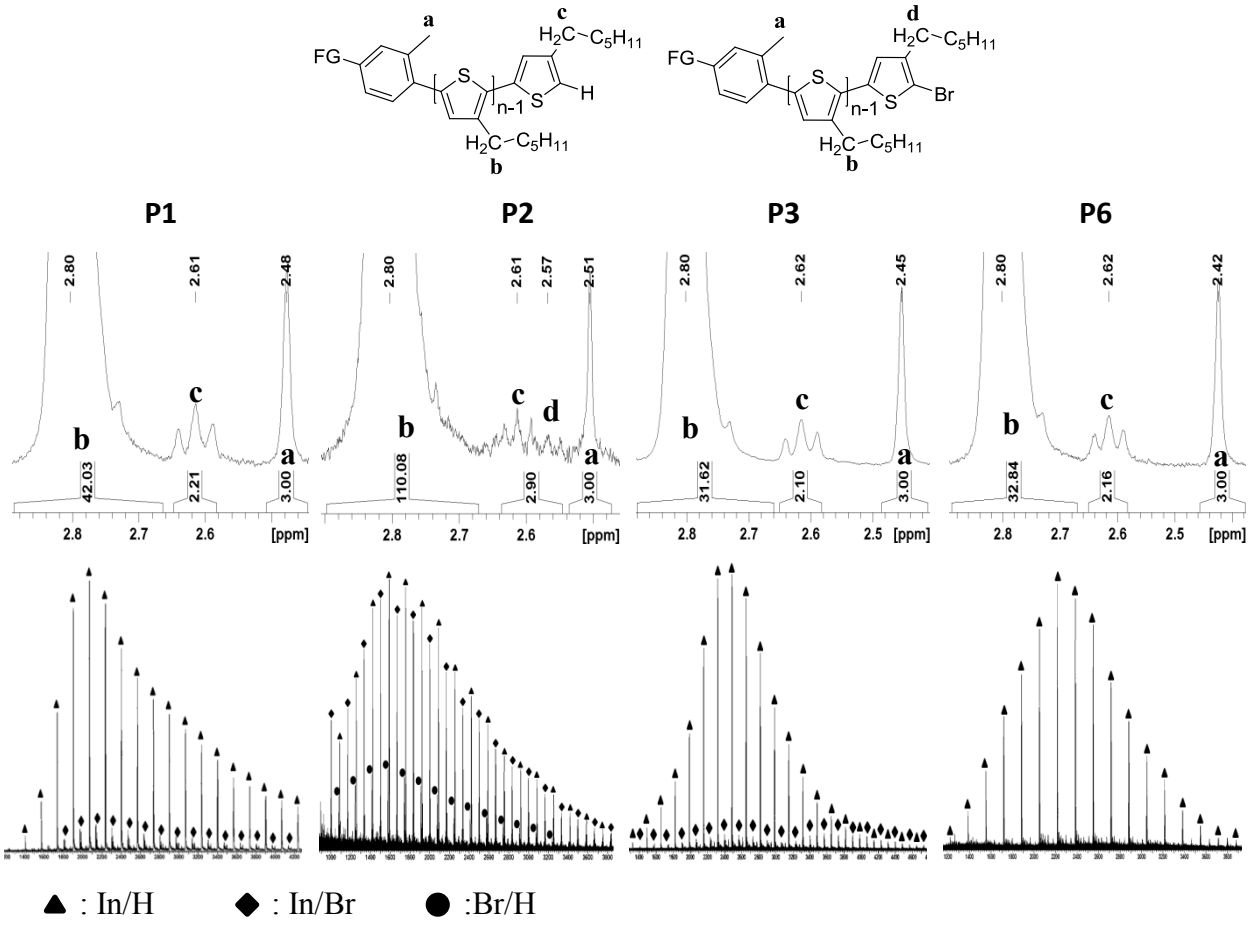


Figure 2. Overview of ^{1}H NMR and MALDI-ToF spectra of **P1**, **P2**, **P3**, **P6**.

Compared to P1, the ^{1}H NMR spectrum of P2 (Figure 2) shows an additional triplet at 2.57 ppm (**d**) indicating that there is some Br-termination present. Also the integration values of end-group α-methylene do not correspond to the integration values of the *o*-tolyl (**a**) function of the initiator. This suggests that some of the polymers were not initiated by initiator **6**. Using the integration of the combined end-groups, it was calculated that about 18% of the polymers did not contain the pyridine function (initiation efficiency ~ 82%). In order to calculate the average DP, Equation 1 was used.

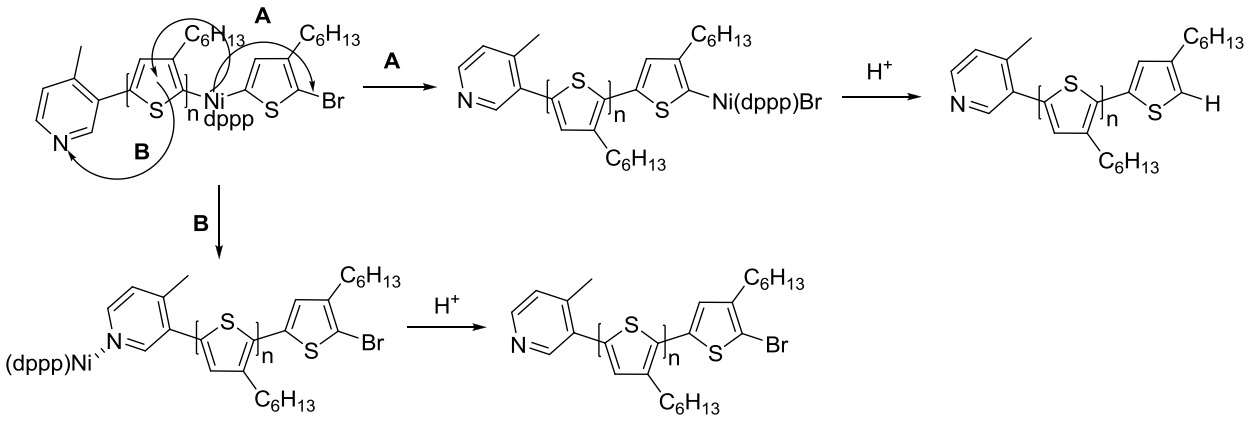
Equation 1. Calculation of DP.

$$DP = \frac{b + c + d}{\frac{c + d}{2} \cdot \frac{a}{3}}$$

MALDI-ToF analysis (Figure 2) reveals high degrees of pyridine/H and pyridine/Br terminated polymers. These Br-terminated polymers can originate from a strong complexation of the Ni-entity with the pyridine-moiety. This strong interaction between pyridine and Ni(dppp) was previously described by Nanashima *et al*.[8] Based on the polymerization mechanism presented in Scheme 3, we can hypothesize that, after the reductive elimination, the Ni-entity can follow route A to undergo an oxidative insertion at the end of the polymer chain. If the polymerization is terminated with acid, this results in pyridine/H terminated polymer. If the catalytic moiety walks back to the initiating group (route B), the strong affinity of the Ni-entity for the pyridine can bind the Ni(dppp) to this unit, resulting in an early termination of polymerization and equipping the polymer chain with a pyridine functionality at one end and a bromine atom at the other end. After decomplexation, the Ni(dppp) can then undergo a reinitiation in monomer yielding H/Br terminated polymer, which were also detected in a minor amount in the MALDI-ToF spectrum. This termination reaction is more likely to occur in the

very early stages of the polymerization (as the Ni(dppp) does not have to walk too far), yielding oligomers that are likely to be removed in the purification steps. As a consequence, the molar mass of the resulting polymers is then higher, since more monomer units are available for the polymer chains that were effectively formed. The termination reaction also explains the higher polydispersity.

Scheme 3. Overview of possible polymerization routes, with route A resulting in pyridine/H terminated P3HT and route B resulting in pyridine/Br terminated P3HT.



Similarly to **P1**, the ^{1}H NMR spectum of **P3** (Figure 2) does not show any Br-terminated chains. The α-methylene of the H-terminated thiophene unit is observed at 2.62 ppm (b) and a large peak corresponding to the internal α-methylene protons is present at 2.80 ppm (b). The *o*-tolyl (a) singlet signal is present at 2.45 ppm, whereas the ethyloxy methylenes give rise to two triplets at respectively 2.92 and 4.11 ppm. The methyl groups of the TIPS-moiety are visible as a doublet at 1.14 ppm (Figure S21). The absence of the Br-termination is in line with the controlled nature of the polymerization and the corresponding integration of the a and b signals suggest In/H terminated chains. The average DP is 16. The MALDI ToF spectrum (Figure 2)

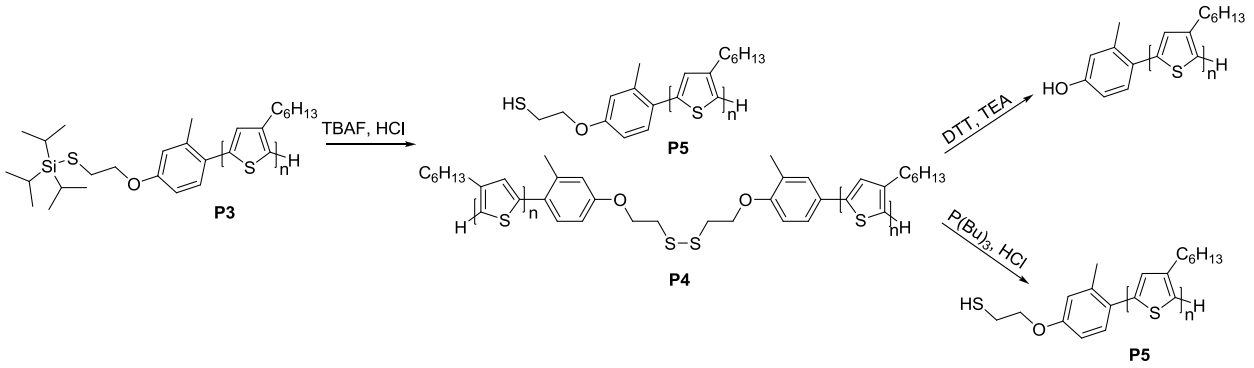
confirms that the vast majority of the peaks originate from In/H terminated polymers, with only a very minor amount of In/Br terminated P3HT.

The best results were found in **P6**: the ^{1}H NMR spectrum did not show any Br-termination. The ratio of both the *o*-tolyl and the α-methylene end-groups suggests complete initiation and a DP of 17 is reached. Besides signals a-c, the *tert*-butyl unit and the methyl protons of the TBDMS protection group are also present (1.00 and 0.23 ppm) (Figure S24). The MALDI-ToF analysis (Figure 2) shows very high degrees of In/H terminated polymer, with hardly any side peaks.

Postpolymerization reactions

The protecting entities of **P3** and **P6** were converted to the actual functional group (Scheme 4). In order to form **P5**, TBAF.3H_2O was added to **P3** in the presence of HCl. Disulfide formation was observed by GPC, as a mixture of disulfide **P4** and some **P5** was formed. An additional reduction step was thus required. In a first attempt, dithiothreitol (DTT) in the presence of triethylamine (TEA) was used. However, this led to a side reaction where a phenol was formed instead of a thiol. Alternatively, tributylphosphine was used in the presence of HCl to prevent this side reaction. GPC confirmed the successful reduction of the disulfides to **P5** (Figure S26).

Scheme 4. Postpolymerization deprotection of **P3** to **P5**.



The deprotection was also demonstrated on the basis of MALDI-ToF analysis, which shows a small amount of phenol-P3HT and a complete disappearance of unprotected **P3** (Figure 3). Finally, the deprotection and reduction reactions were also monitored with ^{1}H NMR (Figure 3) by observing the shift of the resonance signals of the methylenes neighboring the S and O atoms. In this way, both the deprotection and reduction could unambiguously be monitored. Note that the signal at 2.91 ppm (originating from the methylene next to the thiol) changed from a triplet to a quartet due to the coupling with the thiol proton.

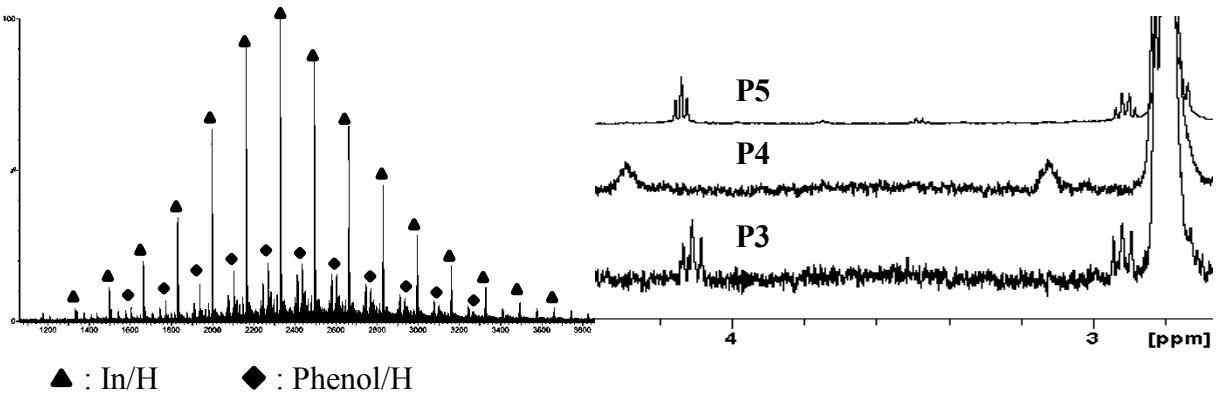
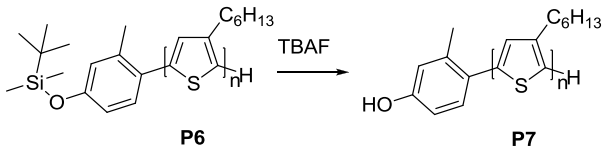


Figure 3. MALDI-ToF spectrum of **P5** and ^{1}H NMR spectra of deprotection.

For the deprotection of P6 to P7, TBAF.3H2O was used (Figure 3). MALDI-ToF analysis shows a successful deprotection, which is also confirmed by the disappearance of the signals at 1.00 and 0.23 ppm in the ^{1}H NMR spectrum (

Figure 4).

Scheme 5. Postpolymerization deprotection of **P6** to **P7**.



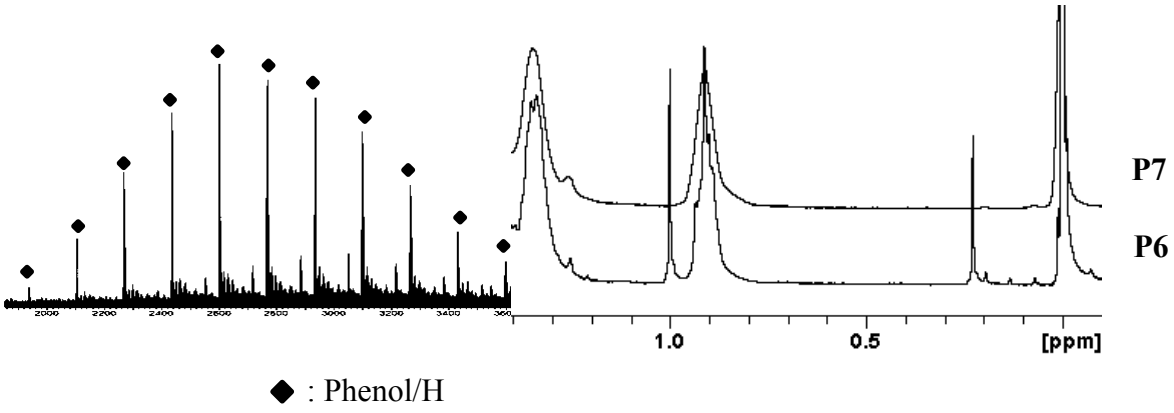


Figure 4. MALDI-ToF spectrum of **P7** and ^{1}H NMR spectra of deprotection.

Synthesis of the hybrid materials

The following part of the present work concerns the preparation of original hybrid materials constituted by the prepared P3HTs and different NPs. As mentioned earlier, the choice of the functional groups was motivated by the fact that a very broad variety of NPs can be covered. Indeed, metal oxides (here superparamagnetic Fe_3O_4) are likely to be decorated using phosphonic ester. Sulfides and selenides (CdSe/ZnS quatum dots) are compatible with pyridines, whereas noble metals (Au)-based NPs are of course likely to be sensitive to sulfides and phenols.

The preparation of the hybrid materials can rely on two different strategies. The first method consists of a transfer reaction in which the functionalized P3HT chains are sonicated in the presence of the NPs stabilized with an organic shell, together with a phase transfer agent. The

mixture is then centrifuged or magnet-assisted precipitated to sediment the hybrids. The process of sedimentation and redispersion is repeated several times in order to obtain a purified hybrid. The second method is the *in situ* formation of the hybrids. The NPs are then synthetized from the corresponding salt in the presence of the functionalized P3HT chains. The CPs act directly as a stabilizer for the formed NPs.

Thus, the first hybrid material (**H1**) is composed of **P1** in combination with Fe_3O_4 NPs. *N*-octylamine coated Fe_3O_4 NPs were synthesized using a modified forced hydrolysis method.[49] The **P1** chains were added to the dispersed NPs and *N*-octylamine was gradually replaced by the functionalized polymer chains. In order to prove that the phosphonic ester functionality interacts with the surface of the Fe_3O_4, hereby anchoring the CPs onto the NP surface, FTIR spectrometry was employed. The IR spectrum (**Figure 5**) showed a shift in the P-OR vibration frequencies from the phosphonic ester functionality from 1028 and 1055 cm^{-1} (**P1**) to 1056 and 1079 cm^{-1} (**H1**). Also the P=O vibration changes: the wavenumber shifts from 1250 cm^{-1} (**P1**) to 1222 cm^{-1} (**H1**).

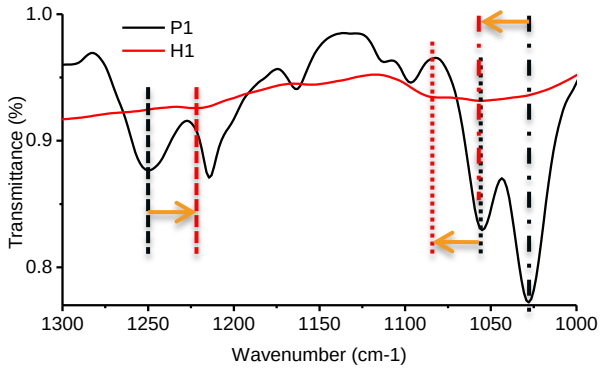


Figure 5. FTIR spectra of **P1** (red) and **H1** (black). The peak shift is indicated with the dashed lines and arrows.

For the synthesis of the second hybrid (**H2**) the two components, respectively **P2** and the quantum dots (CdSe/ZnS), were combined. **H2** was purified by centrifugation and analyzed with FTIR (Figure 6). From the FTIR spectrum it is clear that there is a shift for pyridine entity: from 1561 and 1510 cm^{-1} (**P2**) to 1540 and 1492 cm^{-1} (**H2**).

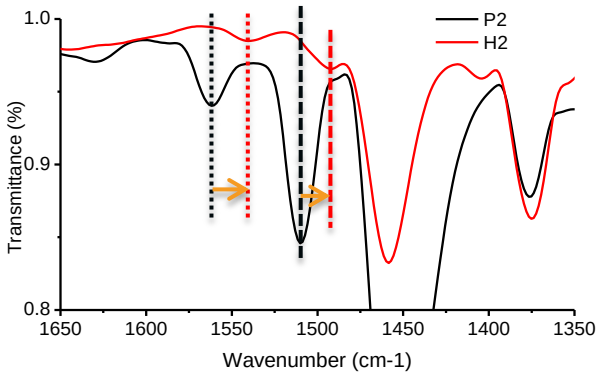


Figure 6. FTIR spectra of the pyridine-P3HT (**P2**) (red) and corresponding hybrid (**H2**) (black). The peak shift is indicated with the dashed lines and arrows.

The synthesis of the third hybrid material uses the thiol functionalized P3HTs (**P5**) and Au NPs.[50] An aqueous solution of citrate stabilized NPs was added to a chloroform solution of **P5** in order to form **H3**. The capping of the CPs onto the Au NPs was examined with UV-vis spectroscopy (Figure 7). The spectrum of **H3** consists of two absorption peaks : one at 435 nm from the P3HT chains and a second absorption peak around 590 nm originating from the Au NP. A clear shift in the Au plasmon band is observed in the hybrid **H3** compared to the citrate stabilized Au NP, indicating the interaction of the thiol functionality of the P3HT chains with the surface of the NPs, hereby forming the hybrid material **H3**.[53–55] Compared with **H4** (see further), the fraction of Au nanoparticles is less in **H3**.

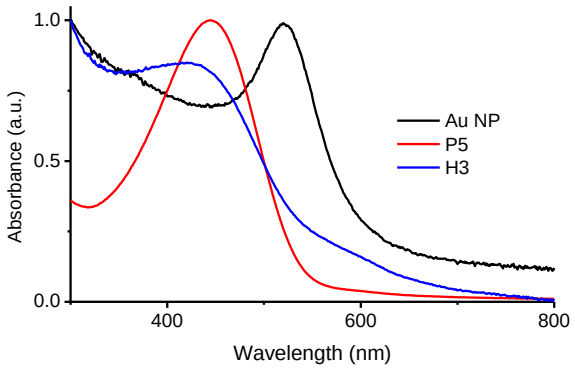


Figure 7. UV-vis spectra of the Au NPs (black), **P5** (red) and the hybrid **H3** (blue).

The last hybrid (**H4)** is formed using a modified Brust-Schiffrin method.[56] With this method, Au NPs are formed from $HAuCl_4$ in the presence of the **P7** chains. In this way the CPs are *in situ* anchored onto the surface and no transfer method is needed. To have evidence for the anchoring of the P3HTs onto the surface of the NP, UV-vis measurements were performed (Figure 8). The red curve represents the **P7** and blue curve results from the hybrid material **H4**. Again, absorption bands of both P3HT (435 nm) and Au NP (550 nm) are present. Note that synthetized Au NPs will not be formed or will cluster if the **P7** chains are not capable of stabilizing the surface of the NPs.

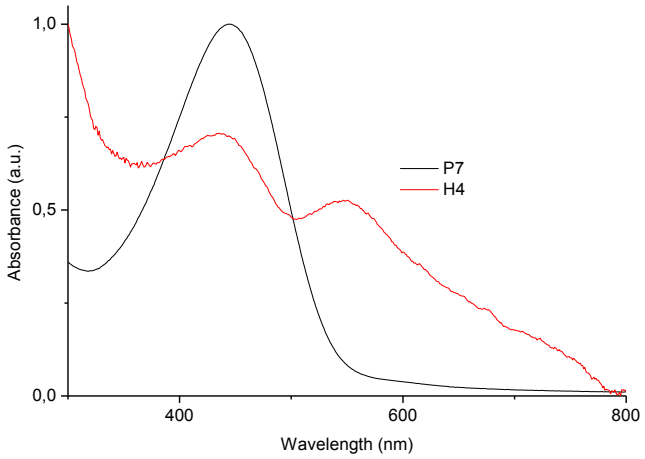


Figure 8. UV-vis spectra of the **P7** (black) and the hybrid **H4** (red).

CONCLUSION

In conclusion, we succeeded in preparing four different functionalized air-stable Ni-initiators, including a phosphonic ester, pyridine, protected thiol and protected phenol. We have shown that these initiators polymerize P3HT with perfect degrees of functionalization and strong control over the polymerization, except for the pyridine functionalized initiator. Furthermore, postpolymerization deprotection reactions yielded the corresponding functional groups with high efficiency. Finally, these functional groups were used to synthesize hybrid materials consisting of different NPs anchored with P3HT.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of all new compounds. ^{1}H NMR and MALDI-ToF spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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